# KINETICS OF RESINIFICATION OF FURFURYL ALCOHOL IN ACIDIC BUFFER SOLUTIONS

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## ABSTRACT

*Kinetic informations on the resinification of furfuryl alcohol have been derived from the rate of increase of colour intensity measured with a photoelectric colorimeter. the resinification being carried out isothermally in McIlvaine's aqueous buffer solutions in the pH range 2·2–3·4. The activation energy for resinification is found to increase exponentially with pH. The time required to reach the extent of reaction at which a resin layer separates out from the aqueous solution increases with increasing pH and decreases with increasing temperature. An exponential expression relating the time of separation with pH and temperature has been derived.*

## 1. INTRODUCTION

Polymerisation of furfuryl alcohol in the presence of acid catalysts yields thermosetting resins, known as furan resins, having exceptional resistance to acids, alkalies, chemicals and solvents. Furan resins have thus gained a variety of applications. There are numerous patents covering the methods of preparation and a wide variety of applications of furfuryl alcohol resins. Several reviews [1–5] of the properties and uses of these resins have appeared. Relatively little is known however of the chemistry of polymerisation of furfuryl alcohol. Dunlop and Peters [6] reviewed the published literature up to 1951. Barr and Wallon [7] reported the chemical composition of furfuryl alcohol resins. Very little has been reported in the literature on the polymerisation kinetics of furfuryl alcohol because of difficulties involved in such a study as discussed below.

The degree of conversion in polymerisation reaction is usually determined by measuring the unconverted monomer. Though furfuryl alcohol can be estimated chemically by bromine oxidation method [8], the method cannot be used to estimate furfuryl alcohol in mixture with its resinification products, since the latter also react with bromine. A physical method of analysis is therefore called for. The polymers of furfuryl alcohol are yellowish brown in colour and the intensity of the colour increases with the extent of reaction. This should then provide a means of obtaining a measure of the rate of resinification from colorimetric meaurements. An attempt has been made in the present work to use this method in studying the kinetics of resinification of furfuryl alcohol.

The highly exothermic nature of the acid-catalysed polymerisation of furfuryl alcohol poses an additional problem since it makes it difficult to maintain isothermal conditions during resinification. In the present work, isothermal conditions were achieved by carrying out the reaction in a stirred reactor jacketed with a boiling liquid.

Since the low polymers of furfuryl alcohol are only partly soluble in water, polymerisation of furfuryl alcohol either in pure state or in aqueous solution results in separation into two layers. Thus in aqueous medium, kinetics of the resinification process cannot be studied beyond a certain degree of conversion at which emulsification occurs.

## 2. EXPERIMENTAL

### *Materials*

The common impurities in furfuryl alcohol are furfural and polymers formed by resinification of furfuryl alcohol. The amount of furfural in furfuryl alcohol can be determined by the sodium bisulphite method [9]. The cloud point test [9] is a measure of the amount of polymer present. For commerical furfuryl alcohol the cloud point should not exceed 10° C. The furfural content of BDH (England) Technical Grade furfuryl alcohol, as determined by the bisulphite method was 0·14% and the cloud point was 8·5° C. For the present work pure furfuryl alcohol was obtained by vacuum distillation of the technical grade material. The cloud point was 4·5° C and its purity as determined by chromatographic analysis was more than 99%.

### *Apparatus and Procedure*

A diagrammatic sketch of the reactor set-up is shown in Fig. 1. The reactor consisted of two round flasks, one inside the other. The inner

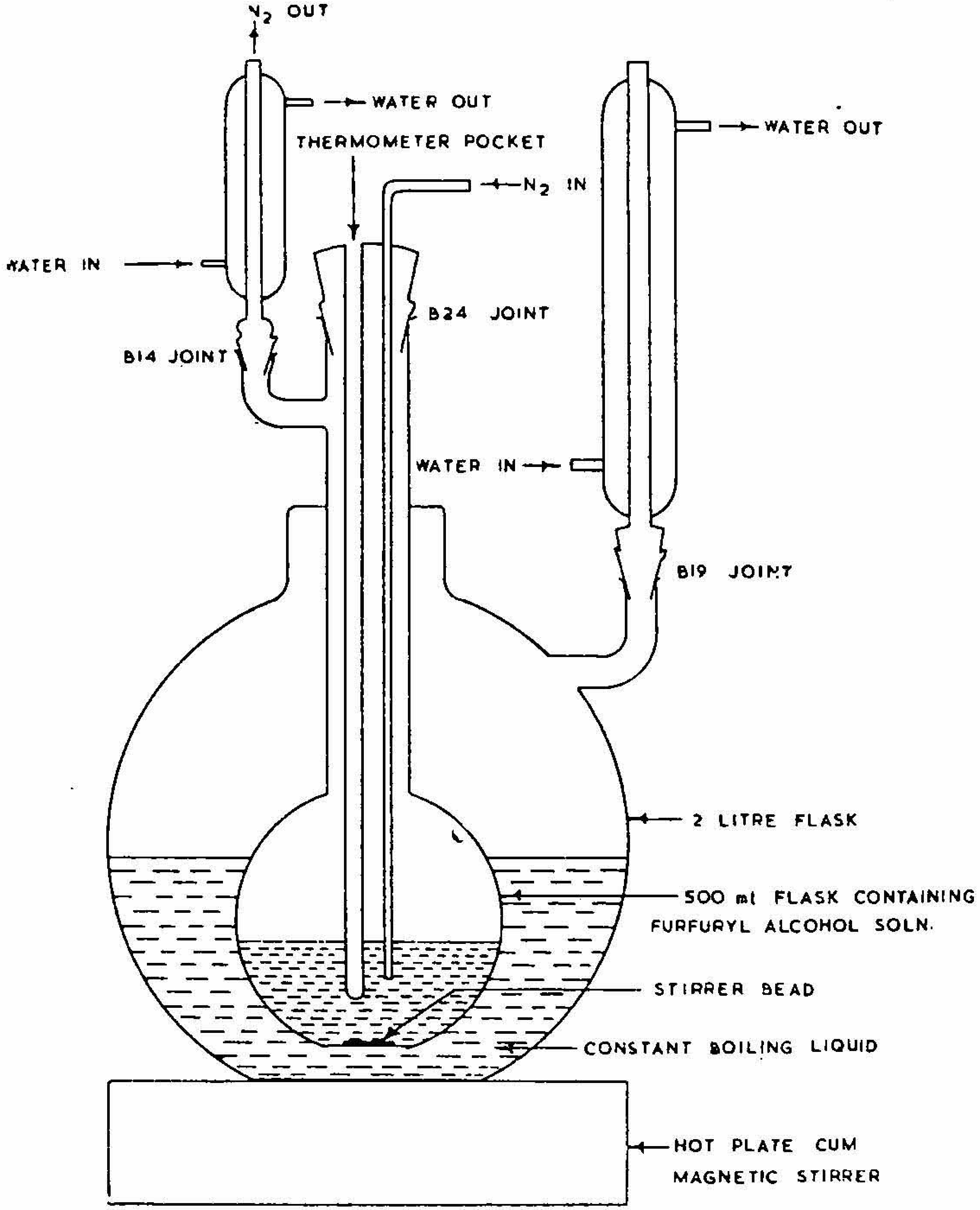

FIG. 1. Reactor for isothermal resinification of furfuryl alcohol.

flask, which contained the reaction mixture, was provided with a vertical water-cooled condenser, a thermometer pocket and an inlet for nitrogen. The reaction mixture was blanketed with nitrogen and stirred with a magnetic stirrer. The outer flask, also fitted with a water-cooled condenser, served as a jacket for the constant boiling liquid used as the heating medium.

The outer flask was heated with the help of a hot plate. In order to prevent a direct transfer of heat from the hot plate to the reaction mixture, a gap of about 5 mm was kept in between the bottoms of inner and outer flasks. The reaction mixture was maintained at a constant temperature by keeping a suitable liquid in the outer jacket at its boiling point and under total reflux.

Acid-catalysed resinification of furfuryl alcohol is also accompanied by a side reaction in which furfuryl alcohol reacts with water to form levulinic acid [6] causing a lowering of pH. Since the rate of resinification is greatly influenced by the pH of the reaction mixture, for kinetic studies a constant pH should be maintained during the period of reaction. An acidic buffer solution instead of a pure acid was therefore used to catalyse the resinification of furfuryl alcohol.

A 50% (by vol.) solution of furfuryl alcohol in McIlvaine's aqueous buffer [10] prepared by mixing calculated volumes of $Na_2HPO_4$ and citric acid solutions of known strengths was used. The actual pH of the mixture was measured with a pH meter. The acidic component (citric acid) was added when the solution in the reaction flask reached a constant temperature, almost equal to the boiling temperature of the liquid in the outer flask. The reaction period was reckoned from the moment the acidic component was added. Samples of the reaction mixture were drawn at different intervals of time and their percentage transmission (relative to that of the initial reaction mixture as 100) was quickly measured using a Systronics Photo-electric colorimeter Type 101 fitted with Ilford blue filter. A stream of purified nitrogen was constantly passed over the reaction mixture in order to prevent entry of air during sampling. The process was continued till the clear solution became cloudy due to separation of resin layer. The time required to reach this stage was noted. The resinification reaction was conducted at different pH levels and at different temperatures, Suitable solvents were used in the jacket to obtain desired temperatures,

## 3. RESULTS AND DISCUSSION

### *Order of Reaction*

Percentage transmission ($T_r$) has been plotted against reaction time ($t$) on a semilogarithm plot (Figs. 2 to 4) for different pH and temperature levels. It is interesting to observe that in each case the plot consists of two linear regions, I and II, having different slopes. For linear region I we can therefore express $T_r$ as a function of $t$ in the form

$$T_r = 100 \exp(-kt) \tag{1}$$

where $k$ is a constant, given by the slope of the plot.

Assuming that the colour of the polymeric species formed by resinification of furfuryl alcohol is due to the presence of one or more of the same type of chromophoric component characterised by the same extinction coefficient, the percentage transmission data can be analysed [11] to derive some kinetic parameters for the reaction. Defining $I_0$ as the original intensity of light and $I$ as the intensity after absorption, in a path length $l$, by a solution of furfuryl alcohol resins, the dependence of the transmission on the concentration $c$ of the chromophoric component in solution can be expressed by Beer-Lambert law as

$$I/I_0 = \exp(-\epsilon cl) \tag{2}$$

where $\epsilon$ is the extinction coefficient of the chromophoric component.

Since $T_r = (I/I_0) \times 100$, comparison of eqs. (1) and (2) gives

$$\epsilon cl = kt$$

or

$$dc/dt = k/\epsilon l = k' \tag{3}$$

Considering $dc/dt$ as a measure of the rate of resinification of furfuryl alcohol, Eq. (3) is taken to signify that this resinification reaction is of zero order. It may be noted that zero order is often an indication of a complex reaction involving a number of steps in succession.

### *Activation Energy*

The resinification rate constant $k'$ is related to the constant $k$, given by the slope of the linear semi-log plot of percentage transmission *versus* reaction time. The constant $k$ will be called the apparent rate constant.

The apparent rate constants are determined for the regions I and II, shown in Figs. 2 to 4, and are denoted by $k_I$ and $k_{II}$. The values of $k_I$ and $k_{II}$ for resinification of furfuryl alcohol at several pH and temperature levels are recorded in Table I. The time required to reach the stage of separation of resin layer under respective pH and temperature conditions are

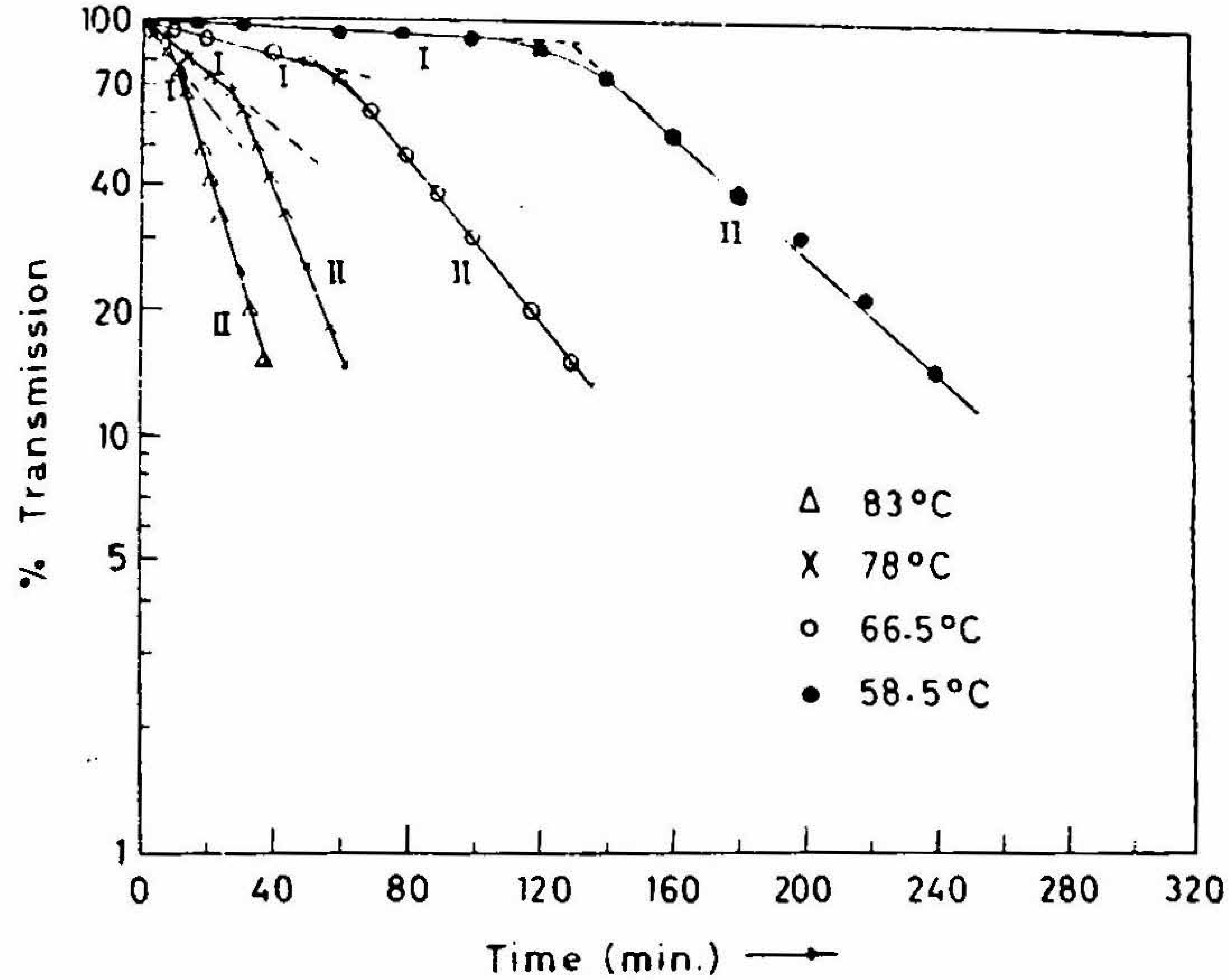

FIG. 2. Semilog plot of percentage transmission *vs.* time of resinification of furfuryl alcohol in McIlvaine's Buffer (50% v/v) at pH 2·280.

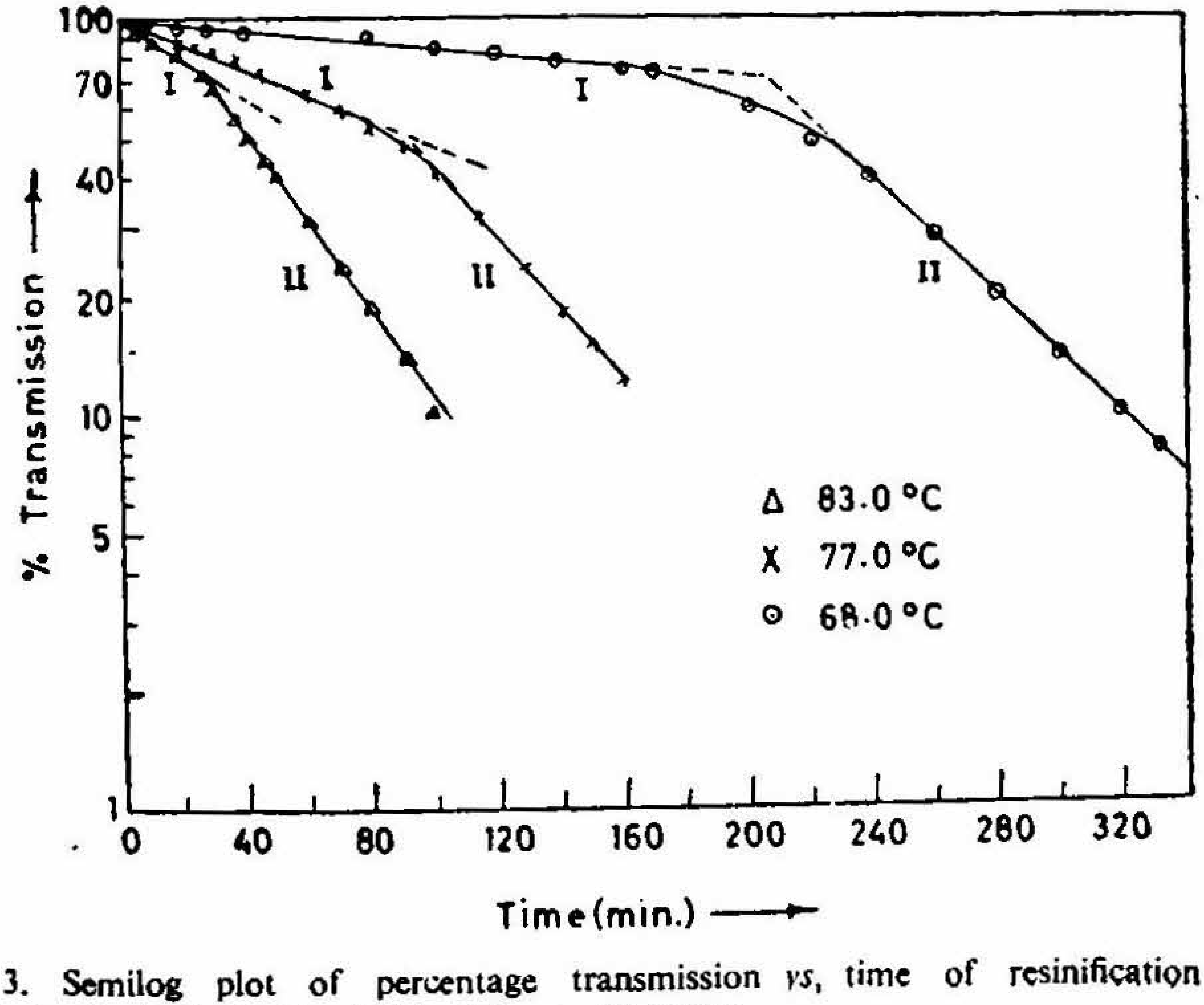

FIG. 3. Semilog plot of percentage transmission *vs*, time of resinification of furfuryl alcohol in McIlvaine's Buffer (50% v/v) at pH 2,840.

TABLE I

*Apparent rate constants and times for phase separation at different temperature and pH levels*

| pH | Temp. (°C) | Apparent Rate Constant | | Time for phase separation $t_s$ (mins.) |
|---|---|---|---|---|
| | | $k_I \times 10^2$ | $k_{II} \times 10^2$ | |
| 2·280 | 83·0 | 2·288 | 5·070 | 46 |
| ,, | 78·0 | 1·376 | 4·374 | 74 |
| ,, | 66·5 | 0·400 | 2·467 | 195 |
| ,, | 58·5 | 0·070 | 2·014 | 370 |
| 2·840 | 83·0 | 1·365 | 2·660 | 155 |
| ,, | 77·0 | 0·567 | 2·053 | 266 |
| ,, | 68·0 | 0·164 | 1·744 | 600 |
| 3·341 | 83·0 | 0·838 | 1·645 | 440 |
| ,, | 77·0 | 0·239 | 1·037 | 800 |
| ,, | 68·0 | 0·084 | 0·866 | .. |

also included in Table I. The reaction rate is evidently faster in region II than in region I and the difference is more marked at lower temperatures.

Assuming that $\epsilon$ is unaffected by temperature, the activation energy for resinification of furfuryl alcohol can be derived from the Arrhenius plot of the apparent rate constant. The Arrhenius plots of $k_I$ and $k_{II}$ corresponding to different pH levels are shown in Figs. 5 and 6 and the respective activation energies are given in Table II. The logarithm of activation energies for resinification in regions I and II is found to have a linear relationship with the pH, as shown by the plots of Fig. 7. The relationships are derived as

TABLE II

*Activation Energy (E) for resinification at different pH levels*

| pH | Activation energy (k cal/ mole) | |
|---|---|---|
| | $E_{I}$ | $E_{II}$ |
| 2·280 | 32·52 | 7·987 |
| 2·840 | 33·65 | 8·500 |
| 3·341 | 35·83 | 9·725 |

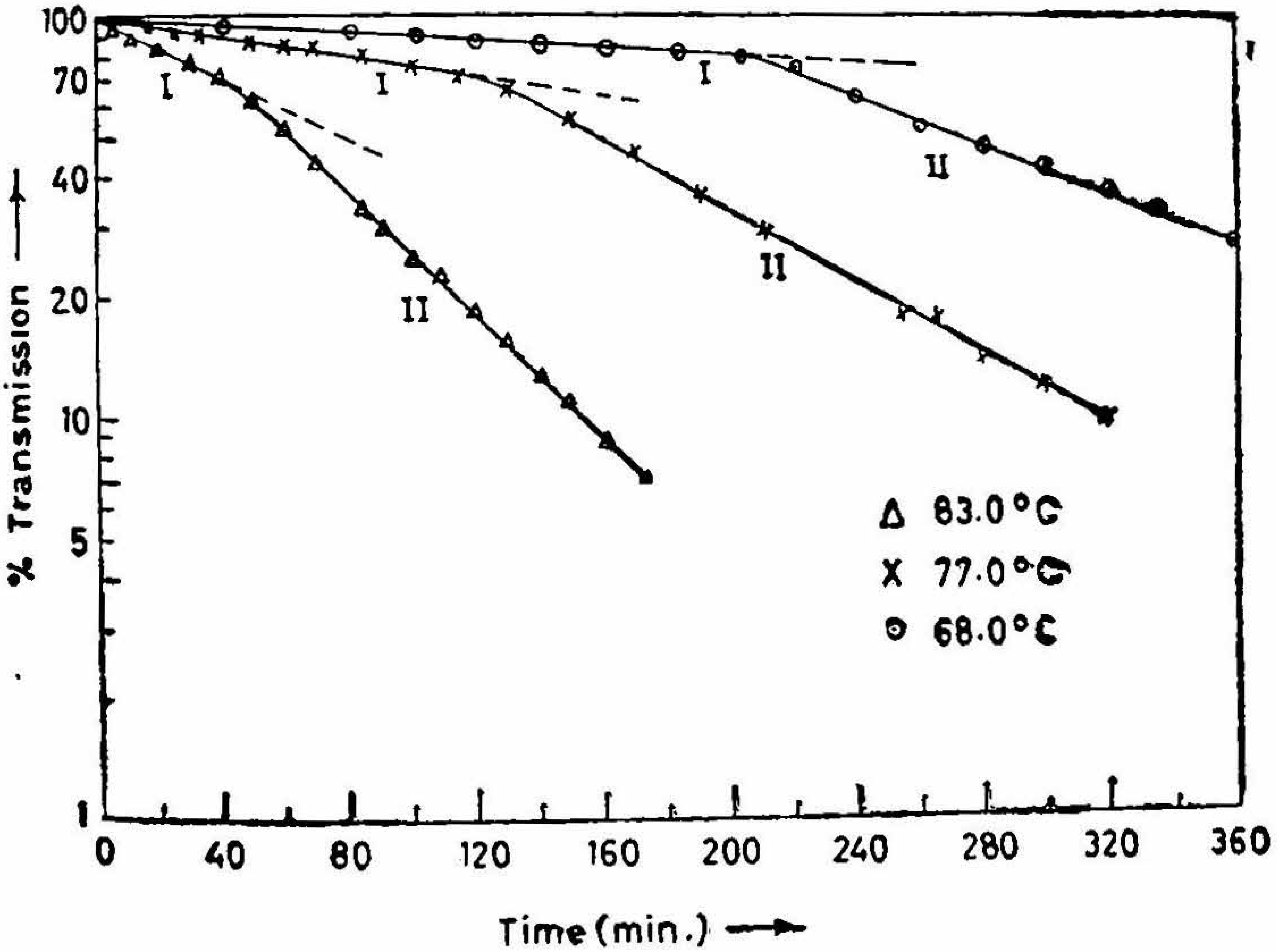

FIG. 4. Semilog plot of percentage transmission *vs.* time of resinification of furfuryl alcohol in McIlvaine's Buffer (50% v/v) at pH 3·341.

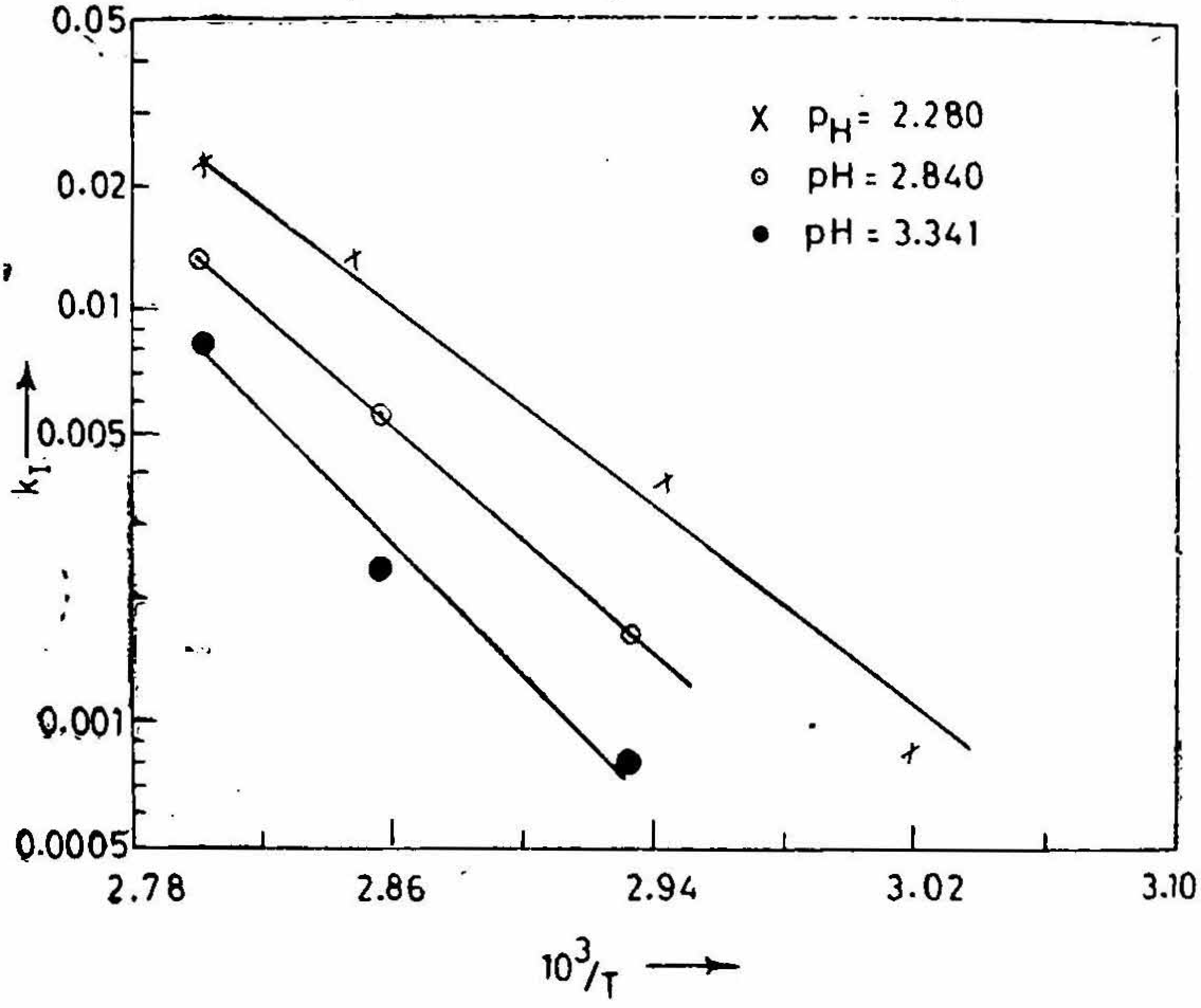

FIG. 5. Arrhenius plot of apparent rate constant $k_T$.

*Region I*

$$E_I = 26 \cdot 3 \exp (0 \cdot 090 \text{ pH}) \text{ kcal/mole} \tag{4}$$

*Region II*

$$E_{II} = 5 \cdot 18 \exp (0 \cdot 1841 \text{ pH}) \text{ kcal/mole} \tag{5}$$

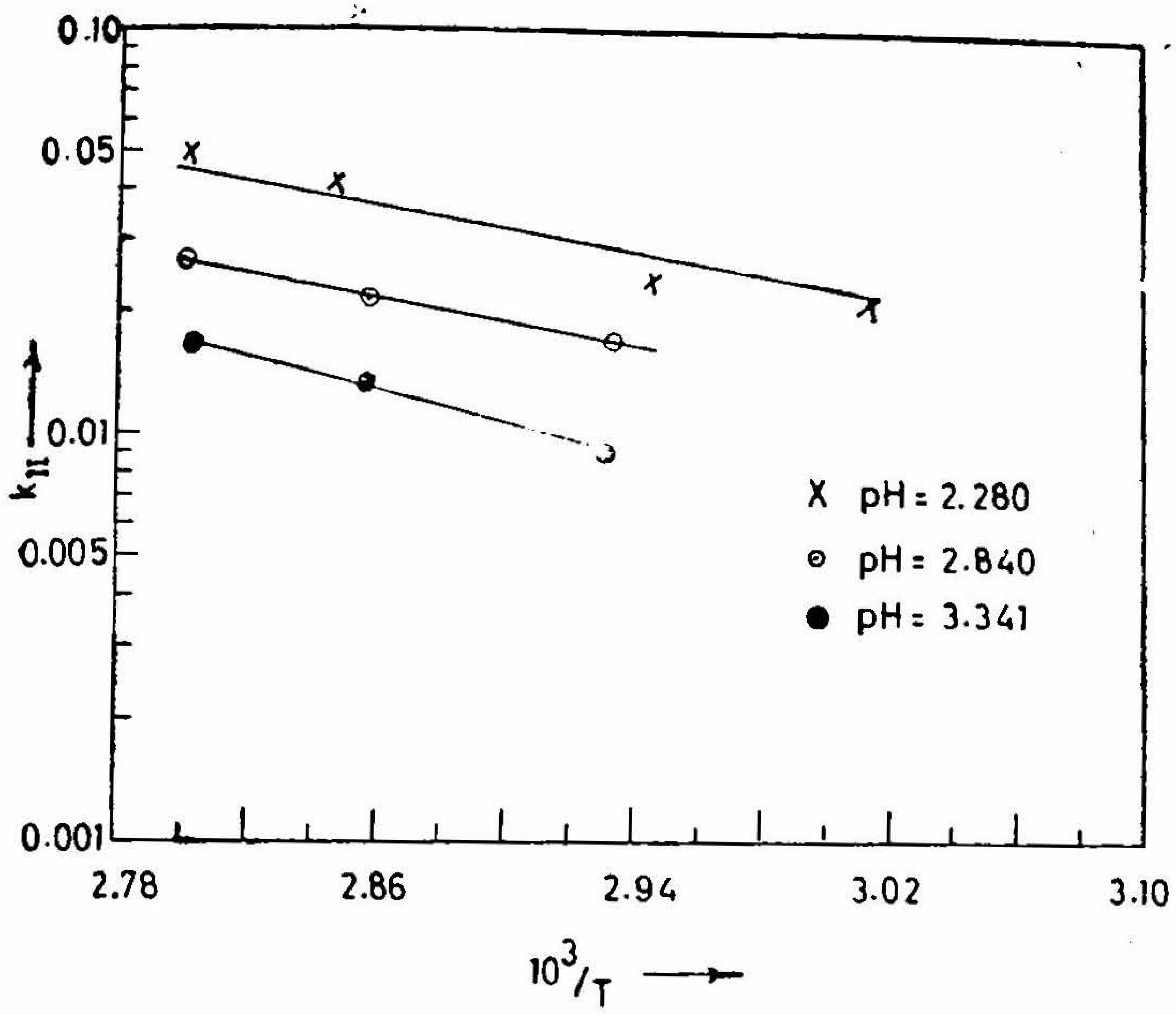

FIG. 6. Arrhenius plot of apparent rate constant $k_{II}$.

### *Time for Phase Separation*

The logarithm of the time for separation ($t_s$) of resin layer bears a direct proportionality to pH. This is in agreement with the observations of Shono and Hachihama [12]. It is further observed that for a given pH, log $t$ decreases linearly with increasing temperature as shown by the plots in Fig. 8. On the basis of the plots of Fig. 8, $t$ has been correlated with temperature ($T$° C) and pH as

$$t_s = 16{\cdot}62 \exp\,[3{\cdot}51\ \text{pH} - (0{\cdot}017\ \text{pH} + 0{\cdot}045)\ T]\ \text{min}. \qquad (6)$$

It should be noted that eqs. (4), (5) and (6) are applicable for furfuryl alcohol resinification catalysed by McIlvaine's buffer (pH 2·2–3·4). The

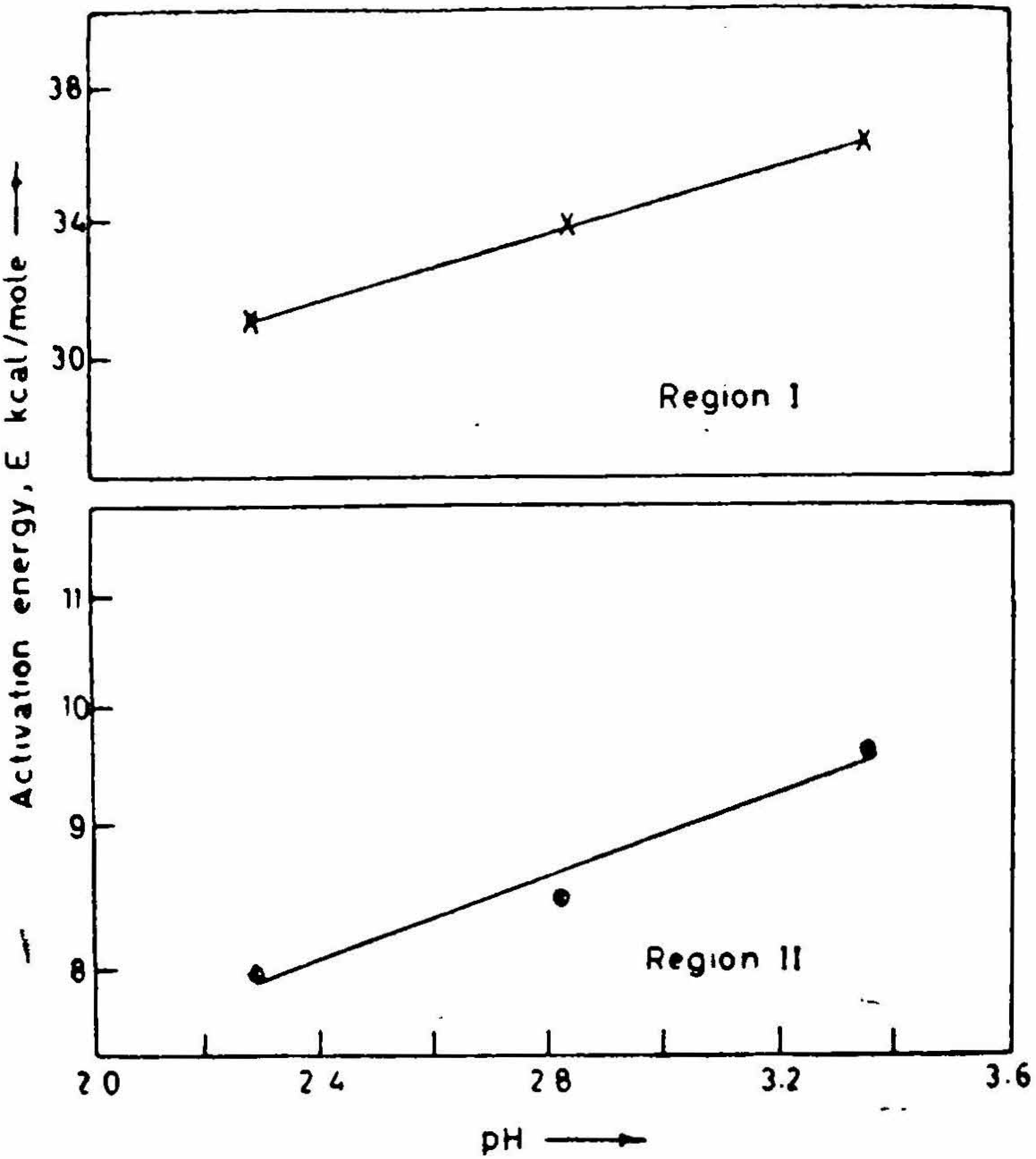

FIG. 7. Semilog plot of activation energy vs. pH.

times of separation calculated from eq. (6) are compared with the experimental values in Fig. 9. The average absolute deviation is less than 5%.

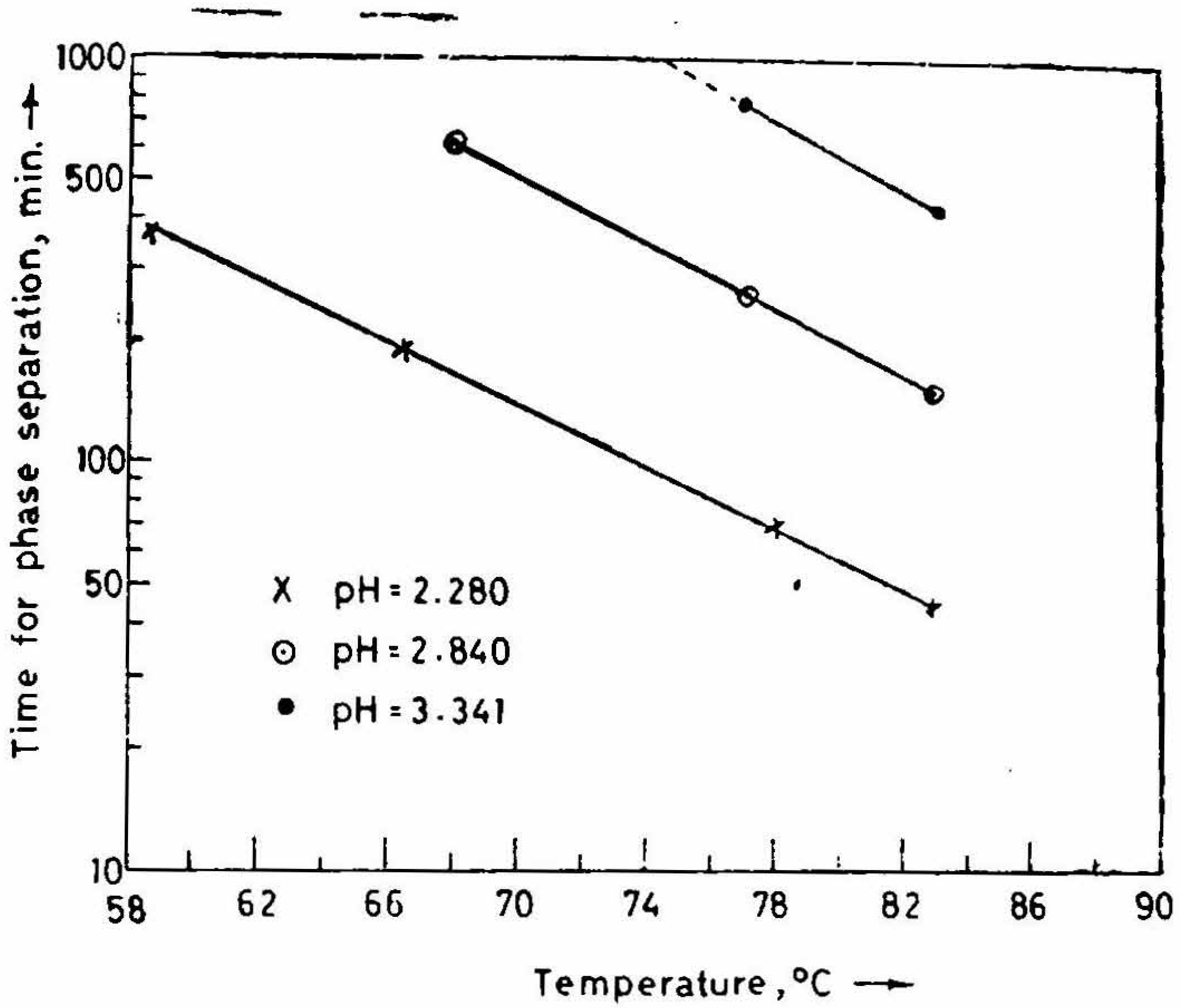

FIG. 8. Semilog plot of time for phase separation *vs.* temperature

## 4. SUMMARY AND CONCLUSIONS

The resinification of furfuryl alcohol in McIlvaine's aqueous buffer solution at different temperature and pH levels in the range 2·2–3·4 has been followed colorimetrically. The analysis of the colorimetric data reveals a zero-order kinetics for the resinification reaction. The resinification is marked by two constant rate periods. The initial period of slow rate of reaction is followed by a period of higher rate of reaction.

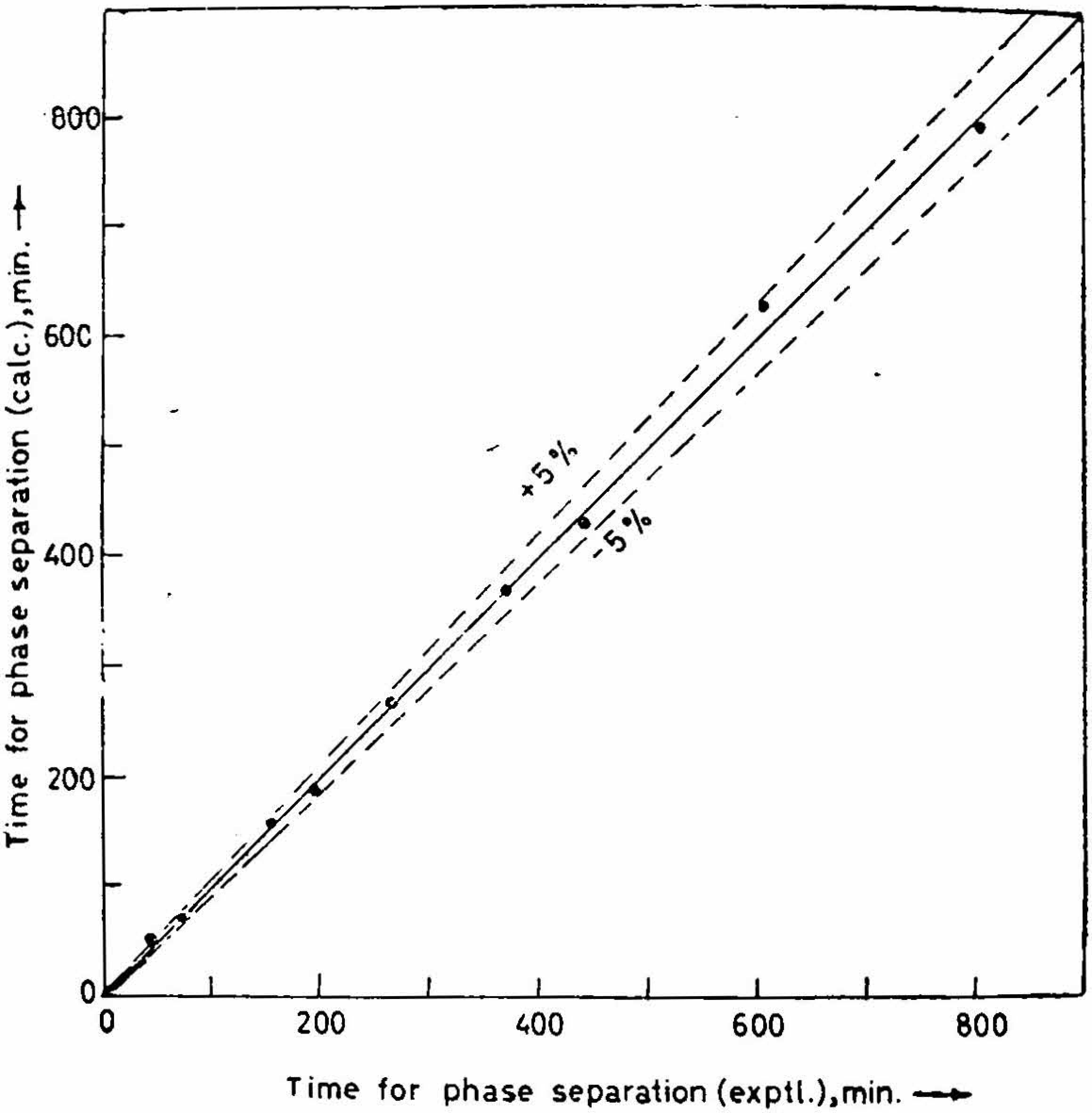

FIG. 9. Time for phase separation: calculated *vs.* experimental.

However, the activation energy for resinification is always higher in the initial period than in the later period. This may be indicative of a shift in the reaction mechanism to a favourable one after an initial period of reaction. The logarithm of the time for separation of resin layer, and hence that of the reciprocal reaction rate, increases linearly with pH. The logarithm of the activation energy also shows a similar variation with pH.

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